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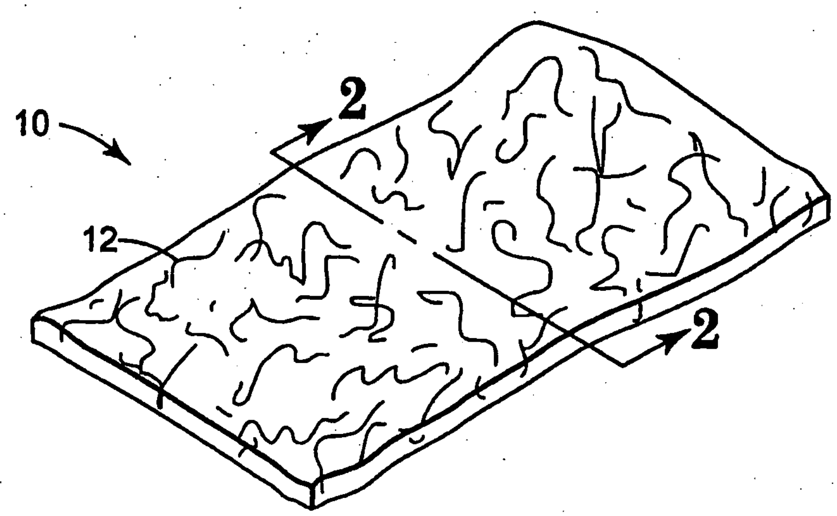

(57) Abstract

Vividly colored absorbent articles useful as wiping articles and a method for their manufacture. A preferred article is characterized by (a) a nonwoven web comprised of organic fibers having a plurality of pendant hydroxyl groups; (b) a binder comprising a cross-linked polyvinyl alcohol and a hydrophobic polymer coated on at least a portion of the fibers, (c) pigment distributed within the binder.

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POLYVINYL ALCOHOL BASED NONWOVEN ARTICLES WITH VIVID COLORS AND METHODS OF PRODUCING SAME

The invention relates to durable, absorbent, colored, nonwoven wiping articles made with a polyvinyl alcohol based binder and to methods for the manufacture of such articles.

Background of the Invention

Wiping articles made of natural chamois, a highly absorbent leather derived from the hides of goat-like antelopes (e.g., from chamois) or other animals, are commonly used in the polishing or drying of certain objects such as automobiles after washing. The absorbent properties of natural chamois have also been emulated in "synthetic chamois", and synthetic chamois articles or wiping articles are known and are commercially available. These synthetic articles are formed, for example, by binding a nonwoven web of fibers with a binder. The fibers may comprise, for example, polyvinyl alcohol (PVA) -- based fibers bound together with a crosslinked PVA binder. Published PCT Application WO 94/28223 describes highly absorbent wiping articles comprised of a nonwoven web bonded with crosslinked PVA binder resins. Other known synthetic chamois are made by bonding nonwoven fibers with an acrylic latex binder. Suitable acrylic binders typically include functional groups to render both the binder and the finished wiping article hydrophilic. Although these acrylic based wiping articles are comparatively inexpensive to make, they often experience undesirably high drag when used in many wiping applications.

Binders made with chemically crosslinked PVA provide some distinct advantages when incorporated in a synthetic wipe. For example, PVA binders increase and improve the properties of a dry wipe by providing a non-linting wipe surface, good mechanical strength, and desired hydrophilic properties. Moreover, PVA binders may be cured in the presence of colorants to generate colored wiping articles.

In the manufacture of synthetic chamois or wiping articles, coloration of the wipe is generally desired for aesthetic reasons as well as for practical or functional reasons. Certain colors, for example, are effective in hiding stains on the surface of the wipe. Additionally, some countries have developed color coding systems for consumer items, including wiping articles, wherein the color of the article designates an intended area of use such as red for use in bathrooms, green for use in kitchens, and the like. In the coloration of these articles,

the use of pigments is generally preferred over dyes because pigments offer greater resistance to fading in the presence of cleaning chemicals.

Commercially available PVA based wiping articles are currently colored in pastel shades achieved either by the addition of pigment or as a result of acid discoloration during manufacture. The use of pigments to provide more vividly colored PVA based wiping articles, however, has generally been unsuccessful because these wiping articles have consistently experienced pigment loss, referred to as "color bleed", when the wipe is exposed to water, especially in the presence of soaps or detergents. . The color bleed phenomenon is attributed to the loss of certain pigment particles that are not adequately retained by the binder resin, but are readily released during the wringing or soaking of the wipe, especially in soapy water. The noticeable loss of pigment from these articles is aesthetically undesirable, and the pigment lost from the article may damage (e.g., stain) the surface being wiped. Although the color bleed problem may be avoided by extensive washing of the wiping article prior to its packaging and use, this additional preparation is costly and may damage the wipe. Consequently, there is a need to solve the problem of color bleed in PVA based wiping articles by providing a means for the retention of pigments in the wipe without prewashing the article prior to use.

It is desirable to provide a solution to the foregoing problem and fill a longfelt need by providing PVA based wiping articles with bright vivid colors. It is desirable to provide these wiping articles by a coloration process utilizing pigments, resulting in an article that does not experience noticeable color bleed when exposed to water, including water containing soaps or detergents. It is also desirable to provide a method for the manufacture of these wiping articles.

Summary of the Invention

The present invention provides vividly colored absorbent articles particularly useful as wiping articles and a method for their manufacture. The articles provide excellent wiping performance, but experience no significant color bleed during use, even when exposed to soapy water or the like.

In one aspect, this invention is an absorbent article comprising a substrate comprised of organic fibers having a plurality of pendant hydroxyl groups; a binder coated on at least a portion of the fibers, the binder comprising a crosslinked polyvinyl alcohol and

a hydrophobic polymer; and pigment distributed within the binder. Preferably, the substrate is a nonwoven web of organic fibers selected from the group of rayon and polyvinyl alcohol. The polyvinyl alcohol (PVA) polymer may be derived from partially or completely hydrolyzed homopolymers and copolymers of vinyl acetate. Preferably, the PVA polymer is a silanol modified PVA. The hydrophobic polymer is derived from a hydrophobic latex emulsion. Preferably, the hydrophobic polymer is a self-crosslinking polymer. The pigment is preferably an organic pigment.

As used herein, the term "absorbent" refers to the ability of a material to absorb a liquid (e.g., water) and to retain the liquid until it is forced out; it also refers to the ability of a material to wet out quickly when exposed to a liquid. "Substrate" refers to a woven, knitted, or nonwoven material. "Fiber" refers to a threadlike structure (In referring to the fibers of webs used to make the articles herein, "linear density" or "fineness" refers to the weight in grams for a given length of a single fiber.). "Crosslinking" refers to chemical reactions of monomers, prepolymers, or polymers (present, for example, in the binder precursor) in which linkages are formed between polymer chains. "Self-crosslinking" refers to a polymer derived from reactants (e.g., monomers), a prepolymer or a polymer that is capable of undergoing a crosslinking reaction without the addition of crosslinking agents. "Pigment" refers to an insoluble material (i.e., a coloring agent) suspended in a medium.

In another aspect, this invention is a method of making an absorbent article, the method by providing a substrate comprising organic fibers having a plurality of pendant hydroxyl groups; coating at least a portion of the fibers with a mixture of a pigment and a binder precursor, the binder precursor comprising polyvinyl alcohol and a hydrophobic latex emulsion; and curing the binder precursor to provide an absorbent article.

In yet another aspect, this invention is an absorbent article comprising a substrate having first and second major surfaces, the substrate comprising organic fibers having a plurality of pendant hydroxyl groups, wherein at least one of the first and second major surfaces is coated with a mixture of a binder comprising a crosslinked polyvinyl alcohol and a hydrophobic polymer and pigment distributed within the binder.

Brief Description of the Drawings

In describing the details of the preferred embodiment, reference is made to the various Figures, wherein:

Figure 1 is a perspective view of a wiping article made in accordance with the invention;

Figure 2 is a cross-section along the lines 2-2 of the article of Figure 1; and

Figure 3 is a schematic diagram of a preferred method of making articles of the invention.

Detailed Description of the Preferred Embodiments

The articles of this invention preferably are comprised of substrates comprising organic fibers having a plurality of pendant hydroxyl groups, wherein at least a portion of the fibers are coated with a mixture of pigment and binder. A mixture of PVA and hydrophobic latex emulsion forms a binder precursor which is cured to form the binder of the invention. The PVA crosslinks due to the presence of a crosslinking agent. The hydrophobic latex emulsion is preferably a self-crosslinking latex, which means that a crosslinking agent is not needed. Surprisingly, the combination of the crosslinked PVA and the hydrophobic polymer derived from the hydrophobic latex emulsion produces a binder that will retain pigment within the finished wiping article, maintain the color of the finished article, and prevent color bleed.

The substrate of this invention may be a woven or nonwoven material. Woven materials include fabrics made by weaving and knitting. Nonwoven materials typically are referred to as mats or webs and are formed by techniques including stitchbonding, air laying, carding, spin bonding, melt blowing, and wet laying.

Preferably, the substrate of this invention is a nonwoven web. More preferably, the nonwoven web has entangled fibers. Entangled fibers are produced by methods such as hydroentangling and needletacking.

The substrate typically will have a thickness ranging from about 0.25 to 2.54 mm (10 to 100 mils), preferably 0.76 to 1.78 mm (30 to 70 mils), more preferably 1.02 to 1.52 mm (40 to 60 mils). The weight per unit area of the substrate preferably ranges from about 50 g/m^2 up to about 250 g/m^2. Woven or knitted webs can be produced to a desired thickness and basis weight. Nonwoven webs can be produced by some techniques in very

thin, lightweight layers. Preferred thicknesses and basis weights for nonwoven webs may be achieved either by carding and crosslapping operations or by air laying followed by fiber entanglement (e.g., hydroentanglement, needletacking and the like). Carded and crosslapped webs may also be entangled. Carded and crosslapped webs are preferred for use in the articles of the present invention.

Referring to the drawings, Figure 1 illustrates an absorbent wiping article 10 according to the invention. Article 10 includes a nonwoven web made of a plurality of fibers 12 at least a portion of which are coated with a mixture of pigment and binder, as is further described herein. As seen in Figure 2, the article 10 (illustrated in exaggerated thickness) includes first and second major surfaces 14 and 16, respectively. Each of surfaces 14 and 16 comprise a combination of calendered and fused binder coated organic fibers. More nonwoven web makes up the middle portion 18 of the article 10. Those skilled in the art will appreciate that an article can be prepared wherein only one of the major surfaces (i.e., surface 14) is coated with binder. The uncoated surface (i.e., surface 16) can be laminated, for example, to another article or a substrate such as a sponge, urethane foam, or the like.

The nonwoven web may be made from any of a variety of hydrophilic fibers, and may include a portion (e.g., less than about 50 percent) of hydrophobic fibers. Hydrophobic fibers include polyolefin fibers such as polyester, polypropylene, and polyamide fibers. Suitable hydrophilic fibers for use herein may be selected from the following fiber types: cellulosic-type fibers such as PVA (including hydrolyzed copolymers of vinyl esters, particularly hydrolyzed copolymers of vinyl acetate), cotton, viscose rayon, cuprammonium rayon and the like; as well as thermoplastics such as polyesters, polypropylene, polyethylene, nylons and the like. The preferred cellulosic-type fibers are rayon and polyvinyl alcohol (PVA) and are commercially available as staple fibers. Suitable rayon fibers are viscose rayon staple fibers commercially available from Courtaulds Fibers Inc. of Axis, AL, under the designations 18552 and T2222. Other suitable rayon fibers are commercially available from Courtaulds Fibers, Inc. under the trade designation "Lyocell" and "Tencel". Suitable PVA fibers include those available under the trade designations VPB 152 and VPB 174 from Kuraray Co. of Tokyo, Japan.

Nonwoven webs containing 100 percent PVA fibers, 100 percent rayon fibers, and blends of PVA fibers and rayon fibers in the ratio of about 1:100 to about 100:1 are

considered within the scope of the invention, and those nonwoven webs having PVA:rayon within the ratio of about 30:70 to about 70:30 are particularly preferred in this invention, because resulting articles exhibit good hydrophilicity and strength, and are soft to the touch.

The fibers used to make the foregoing webs typically have linear densities ranging from about 0.5 to about 10 denier (about 0.06 to about 11 dtex), although higher denier fibers may also be employed. ("Denier" is a unit of linear density or fineness indicating the weight in grams for 9000 meter length of fiber while "dtex" or "decitex" is another unit for linear density indicating the weight in grams for a 10,000 meter length of fiber.) Fibers having linear densities from about 0.5 to 3 denier (0.06 to about 3.33 dtex) are preferred. Fibers having a length ranging from about 0.5 to about 10 cm may be employed as a starting material for the nonwoven web, and fiber lengths ranging from about 2 to about 8 cm are preferred.

The nonwoven web suitable for use in the articles of the invention may be made according to well known methods including air-laying, carding, stitch-bonding, wet laying or melt blowing and spunbonded techniques. A preferred nonwoven web is an open, lofty, three-dimensional air-laid nonwoven material described by Hoover, et al. in U.S. Patent No. 2,958,593, incorporated herein by reference. An air laid web may readily be formed on commercially available equipment such as a "Rando Webber" machine (commercially available from Rando Machine Company, New York) or by other conventional means. (See, for example, Turbak, A. in "Nonwovens: An Advanced Tutorial", Tappi Press, Atlanta, Georgia, 1989).

A major portion of the fibers of the substrate are bonded together with a binder formed by curing the binder precursor. Curing refers to crosslinking reactions in the binder precursor that result in an insoluble binder. Binders suitable in the practice of the present invention comprise a crosslinked PVA and a hydrophobic polymer derived from a hydrophobic latex emulsion. This hydrophobic polymer may also be crosslinked. Preferably, the polymer derived from a hydrophobic latex emulsion is chemically bonded (e.g., by crosslinking) to the PVA in the cured binder. Preferably the binder precursor is comprised of a mixture of dissolved PVA, crosslinking agent, and hydrophobic latex emulsion.

The PVA polymer may be derived from partially or completely hydrolyzed

homopolymers and copolymers of vinyl acetate. PVA polymers having varying degrees of hydrolysis, molecular weights, and comonomers are known and are commercially available, for example, from E.I. DuPont de Nemours Co., Inc. (Wilmington, DE) under the tradename "Elvanol", from Air Products and Chemicals, Inc. (Allentown, PA) under the tradename "Airvol", from Kuraray Chemical KK (Tokyo, Japan) as K, C, HL, and HL series under the trade designations "KL-118, KL-318, KL-506, KM-118, C-118, C-506, C-318, HL-12E, HL-1203, HL-75, HL-1108, R-1130, R-2105 and R-2130" functional polymer. All of these commercial compositions are suitable for use in formulating the binder precusor.

A preferred PVA is a partially or completely hydrolyzed homopolymer or copolymer derived from the copolymerization of first and second monomers. The first monomer may be selected from the group consisting of monomers within the general formula (I)

$$\begin{array}{c} \quad R^2 \\ \quad | \\ R^1\text{—}C\text{=}C\text{—}R^3 \\ \qquad | \\ \qquad X \end{array} \qquad \text{(I)}$$

wherein X is $Si(OR^4OR^5OR^6)$; and

the second monomer is selected from the group comprising monomers within the general formula (II)

$$\begin{array}{c} \quad R^2 \\ \quad | \\ R^1\text{—}C\text{=}C\text{—}R^3 \\ \qquad | \\ \qquad Y \end{array} \qquad \text{(II)}$$

wherein Y is $O(CO)R^7$; and R^1, R^2, R^3, R^4, R^5, R^6 and R^7 are independently selected from the group consisting of hydrogen and organic radicals having from 1 to about 10 carbon atoms.

Silanol modified PVA is particularly preferred in the binder of the invention. Suitable silanol modified PVA may be made by the copolymerization of any one of a number of ethylenically unsaturated monomers having hydrolyzable groups with an

alkoxysilane-substituted ethylenically unsaturated monomer. Non-limiting examples of ethylenically unsaturated monomers having hydrolyzable groups are vinyl acetate, acetoxyethyl acrylate, acetoxyethyl methacrylate, and various propyl acrylate and methacrylate esters. Examples of alkoxysilane-substituted ethylenically unsaturated monomers include vinyl trialkoxysilanes such as vinyl trimethoxysilane, vinyl triethoxysilane, vinyl tripropoxysilane, vinyl tributoxysilane and the like. Vinyl trimethoxysilane is preferred.

One particularly preferred silanol-modified PVA may be produced from the copolymerization of vinyl acetate and vinyl trimethoxysilane, followed by the direct hydrolysis of the copolymer in alkaline solution (see below). A suitable commercially available silanol-modified PVA is that known under the trade designation "R1130" (Kuraray Chemical KK, Japan), believed to contain from about 0.5 to about 1.0 mole percent of the silyl groups as vinylsilane units, exhibit a degree of polymerization of about 1700, and the degree of hydrolysis of the vinyl acetate units being about 99 percent or higher.

In the binder precursor, the PVA is mixed with a suitable crosslinking agent compatible with the PVA. Suitable crosslinking agents include any of a variety of known crosslinking agents including, for example, aldehydes, diisocyanates, polyacrylic acid, and various metal complexes such as chelates of aluminum, titanium, silicon, zirconium and the like. A variety of PVA crosslinkers are described, for example, in *Polyvinyl Alcohol - Developments*, C.A. Finch, Ed., John Wiley and Sons, New York, 1992, pp 272-277, 282-285, incorporated by reference herein. The selection of a suitable crosslinking agent is generally within the skill of those practicing in the field. However, in the selection of a suitable crosslinking for the articles of the invention, consideration should be given to the desired end color of the article. Where vivid colors are desired, crosslinkers requiring strongly acidic catalysts are generally not desirable. Consequently, formaldehyde and other mono- and di-aldehydes are generally not preferred crosslinkers, especially at a low pH.

Preferably the PVA is crosslinked via secondary hydroxyl groups on the PVA backbone using chelating organic titanates as the crosslinking agent. The resultant binder will theoretically further react with hydroxyl groups on the fibers when cured at elevated temperatures. Particularly preferred are "dual" crosslinked PVA polymers wherein an amorphous metal oxide is also used as a crosslinking agent to coordinate with the silanol

groups on the PVA backbone while the aforementioned titanates coordinate with secondary hydroxyl groups, as mentioned. A particularly useful amorphous metal oxide is commercially available under the trade designation "Nalco 8676" (Nalco Chemical, Naperville, IL), an amorphous alumina sol with an average particle size less than about 30 angstroms.

Particularly preferred PVA polymers are those utilizing the aforementioned amorphous metal oxide and a chelating organic titanate crosslinking agent comprising either dihydroxybis(ammonium lactato)titanium (commercially available under the trade designation "Tyzor LA" from E. I. DuPont de Nemours & Co., Inc., Wilmington, DE) or titanium orthoesters (commercially available under the trade designation "Tyzor 131" from E. I. DuPont de Nemours & Co., Inc.).

The theoretical crosslink density for a suitable PVA polymer may range from 1 to about 40 mole percent based on moles of ethylenically unsaturated monomer.

As earlier described the binder comprises a polymer derived from a latex emulsion in the binder precursor. The inclusion of the latex emulsion in the binder precursor has been shown to play an important role in the retention of pigment within the finished article to avoid color bleed when the finished articles are subsequently exposed to soapy water, for example. Surprisingly, retention of pigment within the binder is accomplished by the use of a polymer derived from a hydrophobic latex emulsion without sacrificing the desired absorbency of the finished article.

Without being bound by any particular theory, it is believed that color bleed may result primarily from the loss of the smallest particles of pigment (typically less than about 0.1 micrometer). During the manufacture of articles comprising a PVA binder, binder precursors with low solids content (e.g., less than 15 percent in water) are normally employed. In that binder precursor, the small pigment particles are believed to lose their associated surfactant, causing particle agglomeration. The resulting particle agglomerates are too large to be retained within the cured binder. As a consequence, color bleed results when the agglomerated pigment particles are redispersed into water when the finished article is rinsed with soap and water. Known procedures for mixing pigment have been ineffective in reducing the color bleed phenomenon. The presence of a self-crosslinking hydrophobic latex emulsion has been found to facilitate the association of pigment particles with the latex emulsion. In turn, the pigment particles are readily incorporated into the

binder of the finished article, greatly reducing color bleed. Moreover, this great reduction in color bleed is accomplished by the use of relatively small amounts hydrophobic polymer.

The preferred hydrophobic latex emulsion is one which, when cured, provides a polymer that is associated with the PVA and/or the fibers of the substrate in a manner that resists removal upon exposure to moist or wet conditions, (e.g., exposure to soapy water). Preferably, the latex emulsion is capable of being crosslinked to form a water insoluble crosslinked polymer that is highly resistant to being washed from the finished article. More preferably, the latex emulsion is self-crosslinking and, most preferably, the latex emulsion is both self-crosslinking and capable of covalently bonding with the PVA. To establish if a latex emulsion is hydrophobic, a latex emulsion is coated onto a surface to form a film, then dried and cured. The wetting tension of a surface is related to the hydrophobicity of a surface. This can be measured by using the surface tension of water; or, more specifically, by measuring the angle formed by a drop of water in contact with a surface. For purposes of this invention, a latex is considered hydrophobic if, on a cured film of the latex emulsion, the advancing contact angle of water is greater than about 45°.

The latex emulsion may be present in the binder precursor in amounts ranging from about 0.05 percent up to about 20 percent by weight (based on dry solids). Concentrations above about 20 percent by weight of the latex emulsion in the binder precursor are thought to adversely affect the absorbency of the finished article. Concentrations less than about 0.05 percent are not effective for retaining the pigment in the binder. Preferably, the latex emulsion is present in the binder precursor in an amount from about 1 percent to about 15 percent by weight (based on dry solids). More preferably, the latex emulsion is present in an amount of about 3 percent to about 10 percent by weight (based on dry solids). So that the hydrophobic polymer will not detract from the softness of the finished article, especially when wet, the hydrophobic polymer should have a glass transition temperature (T_g) of less than about 5° C, preferably less than about 0° C, and more preferably less than about -15° C.

Examples of suitable hydrophobic latex emulsions for use in this invention include, but are not limited to, those based on acrylates such as copolymers of butyl acrylate, ethyl acrylate, acrylic acid, methacrylic acid, methyl methacrylate, acrylonitrile, styrene, *N*-methylolacrylamide, etc.; polyurethanes; polyesters; and polyamides. Commercially available latex emulsions useful in the invention include acrylate emulsions available under

the trade designations "Rohamere 132", "Rohamere 1878", "Rohamere 1900-D", "Rohamere 1970-D", "Rohamere 3045", "Rohamere 31-130", "Rohamere 4096D", "Rohamere 587", "Rohamere 84116", "Rohamere 8437", "Rohamere 8464", "Rohamere 8478", "Rohamere 8662" and "Rohamere 87219", all available from Rohm Tech Inc. (Malden, MA). A variety of acrylic latex emulsions having suitable physical characteristics for the practice of this invention are commercially available under the trade designation "Rhoplex" from Rohm and Haas Co. of Philadelphia, PA. Vinyl acetate/ethylene latex emulsions having suitable physical characteristics are available under the trade designation "Airflex" and polyvinyl acetate homopolymers are available under the trade designation "Vinac", both from Air Products and Chemicals, Inc. of Allentown, PA. Preferred hydrophobic latices include styrene -butyl acrylate available under the trade designation "Hycar T-278" from B.F. Goodrich Co. of Akron, OH, and acrylic latices available under the trade designations "Rhoplex E-2744" and "Rhoplex NW-1845" from Rohm and Haas Co. It will be appreciated that other suitable hydrophobic latex emulsions can be used in the preparation of the binder precursor.

The binder precursor comprises a solution, preferably aqueous, of dissolved PVA, crosslinking agent and hydrophobic latex emulsion. The binder precursor may be from about 1 percent to about 60 percent solids by weight, preferably from about 2 percent to about 20 percent solids by weight. The binder precursor is typically prepared by first dissolving the PVA in water, adding crosslinking agents and then adding a hydrophobic latex with stirring.

Crosslinking of the PVA as well as of the latex emulsion should be avoided until curing conditions (i.e., high temperatures) are present. When titanate crosslinking agents are utilized, organic acids such as citric acid may be added to the binder precursor to help stabilize the titanates (e.g., dihydroxybis(ammonium lactato) titanium) in aqueous compositions until the binder precursors are exposed to crosslinking and curing conditions. If acid activated crosslinking agents are employed (for example, aldehydes, or aminoplast resins), then it may be desirable to incorporate a latent acid such as diammonium phosphate into the binder precursor.

Pigments are mixed with the binder precursor. Pigments that are useful in the present invention include inorganic and organic pigments. Inorganic pigment generally refers to a finely divided metallic oxides or sulfides. Inorganic pigments are not soluble.

They may be highly colored for use as coloring agents or, for example, white, for use as an opacifying agent. Organic pigment generally refers to highly colored materials which are carbon-based, rather than metal-based. For the purposes of this invention, an organic compound is a pigment when it imparts a desired color to the article and is not soluble in the solvents used while making or using the articles of this invention.

Preferably, pigments are added to the binder precursor as aqueous dispersions of finely divided particles. The particles typically range in size from sub-micrometer to about 10 micrometers. The dispersions facilitate distribution of pigment within the binder. Suitable aqueous dispersions of organic pigments are available from commercial sources . These include textile and graphic arts pigment grades from companies including Sun Chemical Co. (Fort Lee, NJ), Heucotech Ltd. (Fairless Hills, PA), Catawba Char-Lab (Charlotte, NC), Organic Dyestuffs Co. (Charlotte, NC), Penn Color (Doylestown, PA), and BASF Corp. (Wyandotte, MI). Pigments also may be prepared according to methods well known in the art.

Suitable pigments include, but are not limited to, organic pigments, for example, azo pigments such as soluble or insoluble azo pigments or condensed azo pigments, phthalocyanine pigments, quinacridone pigments, isoindolinone pigments, perylene-perynone pigments, dioxazine pigments, vat dye pigments and basic dye pigments, and inorganic pigments such as carbon black, titanium oxide, chrome yellow, cadmium yellow, cadmium red, red iron oxide, iron black, zinc flower, Prussian blue and ultramarine. In general, organic pigments are preferred, because they do not contain heavy metals, such as chromium, lead, tin and/or barium.

In addition to the above-mentioned components, it may also be desirable to add optional ingredients to the binder precursor. Such optional ingredients include softeners (such as ethers and alcohols), fragrances, fillers (such as for example silica, alumina, and titanium dioxide particles), and bactericidal agents (e.g., quaternary ammonium salts). The inclusion of these ingredients and their relative proportions within the binder precursor will vary depending on the chemical identity of the ingredient and its intended function as will be readily appreciated by those practicing in the field.

In the method of this invention, a substrate having the desired thickness and weight per unit area is provided. At least a portion of the substrate is coated with a mixture of binder precursor and pigment, dried, and heated to cure the binder precursor to form binder

and pigment on at least a portion of the substrate.

Turning now to Figure 3, a method of producing a preferred substrate, a nonwoven web, (as illustrated in Figures 1 and 2) is shown schematically. In the preparation of a nonwoven web, staple fibers are fed via hopper 20 (or other means) into carding station 22. A moving conveyer transports carded web 26 from carding station 22, typically to a crosslapper, not shown, to form a layered web having fibers oriented at various angles relative to the machine direction of carded web 26. Carded web 26 then passes through needle tacking station 28 to entangle the fibers, thus strengthening and consolidating the web, and resulting in needle tacked web 30. Entanglement of the web may alternatively be achieved by means other than needle tacking, such as by hydroentanglement.

Needle tacked web 30 may optionally pass through calender station 32 to achieve a desired thickness, providing calendered web 34 that preferably is not more than about 1.52 mm (60 mils) thick. Calendered web 34 then passes through an immersion bath 36 where a mixture of pigment and binder precursor 37 is applied. Web 34 passes under rollers 38 and emerges as coated web 40. Coating of the web with binder precursor may be accomplished by immersion coating methods as well as by other coating methods known in the art including roll coating, spray coating, gravure coating, transfer coating and the like. During coating, at least a portion of the fibers are coated, and preferably the web is coated on at least one of its first and second major surfaces with a mixture of pigment and binder precursor. In the preparation of articles to be used as hand wiping articles or the like, the web is typically coated on both of its major surfaces. The coating weight (i.e., dry binder add-on weight) is reported as a percentage of the weight of the finished wiping article. The coating weight ranges from about 1 percent to about 95 percent, preferably from about 10 percent to about 60 percent, more preferably 20 percent to 40 percent.

Coated web 40 passes through drying station 42 to form dried web 44. While resident in drying station 42, the web is typically and preferably exposed to an elevated temperature to remove water from the binder precursor and form dried web 44. Drying may be accomplished using heated rollers (i.e., "hot can"), a forced air oven, a radiant panel or other known means. Preferably, drying is uniform throughout the thickness of the web. Depending on the composition of the binder precursor, the type of crosslinking agent used, the amount of water present and the like, web 44 may be suitable for use without further curing.

Typically and preferably, it is desirable to first dry and then cure the binder precursor. This two stage process is accomplished by first drying the web as discussed above. Dried web 44 is then passed through final curing station 46, which is maintained at a temperature higher than the temperature of drying station 42. In the curing station, exposure to the elevated temperature cures the binder to form dried and cured web 48. Drying and curing of the binder precursor may be accomplished by exposing dried web 44 to more than two different temperatures by, for example, performing the drying and the curing steps in an oven having more than two heating zones. Additionally, in drying and curing the binder precursor, both major surfaces of the uncured web preferably are simultaneously exposed to a heat source. Alternatively, although less preferred, the first and second major surfaces of the coated web may be exposed in sequence to the heat source.

Web 48 may then be passed through another set of calender rollers 50, which may used to emboss a pattern and fuse the surfaces of the article. Web 52 generally has a thickness of no more than 1.52 mm (60 mils), and a weight ranging from about 50 g/m^2 to about 250 g/m^2. Calendering of the binder coated web at temperatures from about 5 to about 40°C below the melting point of the fiber may reduce the likelihood of lint attaching to the surface of the articles and will generally provide a smooth surface. Embossing of a textured pattern onto the wiping article may be performed simultaneously with calendering, or in a subsequent step.

Web 52 may then pass through an optional second needling station 54 to perforate the web for decorative or other purposes, after which the web is slit and wound onto take-up roll 56.

Alternatively, web 52 may pass through a hot water (i.e., from about 60 to about 80°C) bath (not shown), and calendared and dried by means of heated rollers as described above, to produced a soft “hand” or feel before being slit and wound up onto take-up roll 56. Another way to achieve a soft feel in final packaged form and to aid in processing is to apply a small amount of water or fungicide solution to the article immediately prior to packaging. The cured article may be laminated or otherwise affixed to another substrate, if desired, such as a sponge, a urethane foam backing or the like. It may be desirable in the applications to use cured articles having a binder on only one of the major surfaces, thus providing an untreated major surface (i.e., a surface free of cured binder) for the application

of adhesives or the like.

The articles of this invention are particularly useful as "synthetic chamois" due to their absorbency and durability. These synthetic wiping articles are useful for cleaning various surfaces. The presence of pigment in the article produces an aesthetically pleasing and functional absorbent wiping article for consumer use. Preferably, the articles are highly colored, producing readily recognizable colored articles which are used for cleaning certain areas (e.g., green for use in kitchens). The articles prepared according to this invention exhibit minimal color bleed due to pigment being lost from the article during use.

The examples illustrate the preparation of webs coated with a binder and a pigment suitable for use as absorbent articles.

MATERIALS DESCRIPTION

In the Examples, certain materials were used which are identified according to the following abbreviations and trade designations.

PREPARATIVE PROCEDURES

The following preparative procedures were used in the preparation of the articles identified in the Examples.

PROCEDURE A (SUBSTRATE PREPARATION)

The nonwoven web was prepared from 50 percent rayon fibers (3.0 d x 6.3 cm, T2222, Courtaulds Fibers Inc. (Axis, AL) and 50 percent polyvinyl alcohol fibers (1.7 d x 5.3 cm, VPB174, Kuraray Co. KK (Tokyo, Japan)). The nonwoven web was prepared by carding and crosslapping and was needlepunched to provide a web with a basis wt. of 162.9 g/m^2 (4.8 oz / yd^2) and a thickness of 1.45 mm (57 mils). For the following examples the web was coated as pieces of dimension 30.5 cm x 38.1 cm (12 inches by 15 inches). In the production of a nonwoven web, there is orientation of the fibers depending upon how it is produced; thus reference is made to the "machine", or down web, direction, in contrast to the "cross web" direction, which is orthogonal to the machine direction.

PROCEDURE B (PVA SOLUTION)

A coating solution was made by heating 9.3 parts polyvinyl alcohol ("R1130" from Kuraray Co. KK) to boiling in 90.7 parts deionized water to dissolve the PVA. Amorphous

alumina sol (0.44 parts, "Nalco 8676" from Nalco Chemical Co.) was added to the PVA solution followed by the addition of 4.4 parts titanate ("Tyzor 131, commercially available from E.I. DuPont de Nemours, Co., Inc., of Wilmington, DE). The resultant solution was cooled and then diluted with deionized water to achieve a solids content of 3.6 weight percent when dried at 121°C (250°F).

PROCEDURE C (BINDER PRECURSOR AND WIPING ARTICLES)

Latex emulsion and pigment were added to the PVA solution in proportions described in the examples, along with additional deionized water as indicated in the examples. The PVA solution and the latex emulsion form the binder precursor. The mixture of pigment and binder precursor was poured onto the substrate and evenly distributed by hand to make a coated substrate. Then the coated substrate was air dried at 65.6 °C (150° F) until dry and heat cured at 149 °C (300° F) for 10 minutes. The amount of the dried and cured polymer (i.e., binder) on the substrate was about 18 weight percent.

TEST METHODS

The following Test Methods were employed in evaluating the wiping articles of the Examples.

COLOR BLEED

Color bleed was determined by first taking a sample of material to be evaluated and placing it in 2 liters of water and allowed to soak for 60 seconds. The sample was then wrung out by hand and the rinse water was collected in a dishpan. The soak and wringing steps were repeated twenty times for each material sample tested. Thereafter, the color hue and intensity of the rinse solution and the dishpan surface were observed and recorded, and the visible absorption spectrum of the rinse water was measured and recorded using a 10 cm path length cell on a UV-visible spectrophotometer.

The rinse solution was then discarded from the dishpan and replaced with 2 liters of fresh water. The sample was wrung out completely and 2 g of detergent (available under the trade designation "Liquinox" from Alconox, Inc. of New York, New York) was placed on the sample and rubbed in lightly over the majority of sample surface. The thus treated sample was placed in the fresh water. The sample was then wrung out by hand with the detergent/water mixture returned to the dishpan. The sample was again soaked and wrung

out a second time and the visible absorption spectrum of the rinse water was measured using a 10 cm path length cell, as previously described.

TENSILE STRENGTH

Samples were prepared for testing by wetting them in water and wringing them out once with a mechanical wringer. Samples were die cut to 2.54 x 15.24 cm (1 x 6 inch).

Tensile strength measurements were made using a tensile tester (Instron Model "TM", obtained from Instron Corp. of Canton, MA), using a procedure modified from that of the test method described in ASTM D 5035-95, "Standard Test Method for Breaking Force and Elongation of Textile Fabrics (Strip Method)". The sample thickness also was recorded. A constant rate of extension was employed, and jaws were clamp-type. Rate of jaw separation was 25.4 cm/min (10 inches/min). The sample was placed into the jaws, set at a 2.5 cm (1 inch) gap, and the cycle was started. The tensile strength (i.e., load) and the elongation at break were measured. The tensile strength is an indication of the stiffness of the sample. Elongation at break is a measure of a load which is applied and increased until the sample breaks. Measurements were done on the samples in machine direction and the cross web direction, as mechanical properties may vary depending upon the direction of orientation.

BLEACH STABILITY

Wiping articles were immersed for 8 hours in a mixture of 286 g of 5.25 weight percent chlorine bleach (household strength chlorine bleach, commercially available under the trade designation "Clorox" from The Clorox Co. of Oakland, CA) in 14 liters of tap water. When the samples were removed from the bleach solution, they were visually evaluated for color fading.

ELMENDORF TEAR TEST

Samples were prepared for tear testing by soaking them for 5 minutes in tepid water and then mechanically wringing them.

Elmendorf tear tests were conducted on 6.35 x 27.94 cm (2.5 x 11 inch) die-cut, notched (20 mm) samples, using an Elmendorf Tear Tester model number 60-32, from Thwing-Albert Co., with a 6.4 kg pendulum. The procedure was modified from that of the

test method described in ASTM D 1424-96, "Standard Test Method for Tearing Strength of Fabrics by Falling-Pendulum Type (Elmendorf) Apparatus". An average of four measurements is reported. Samples were tested in both the machine direction and the transverse direction. The tear tests are indicative of the durability of the absorbent articles of this invention.

ABSORPTION TESTING

Water absorption was determined by first soaking a sample for 15 minutes in tepid water in a dishpan or other container. The sample was then mechanically wrung to remove most of the water. While still damp, 15.2 cm x 20.3 cm (6 inch x 8 inch) square portions of the material were cut. The cut samples were again placed in a dishpan of tepid water and allowed to soak for 15 minutes. A screen was placed under one of the cut samples in the dishpan. After 30 seconds, the screen and the cut sample were lifted from the dishpan, and the sample was removed from the screen with tweezers and immediately placed onto a weighing pan with a quick smooth motion. This operation requires some technique by the analysts and should be practiced until a reproducibility of ± 1 gram is regularly achieved. The balance reading was recorded in grams as Total H_2O Absorbed / No Drip (A). This procedure was repeated for the remaining cut samples.

The thus-treated cut samples were soaked in a dishpan of tepid water for 5 minutes. Thereafter, the samples were removed from the water with tweezers and then hung by one corner using a spring clamp attached to a ring stand. After 60 seconds, each sample was transferred onto the weighing pan with one quick smooth motion. The balance reading in grams was recorded as Total H_2O Absorbed w/ Drip (B). This procedure was repeated for the remaining cut samples.

The cut samples were again placed in a dishpan of tepid water for 5 minutes. Thereafter, each sample was removed from the water and passed through a mechanical wringer at single thickness. The sample was transferred onto the weighing pan with one quick smooth motion, and the balance reading in grams was recorded as Damp Weight (C). This procedure was repeated for the remaining cut samples.

The cut samples were then placed into a vented forced air oven maintained at 49°C (120°F) for at least 12 hours. Up to six samples were removed from the oven at a time and their weight in grams was measured immediately and recorded as Dry Weight (D). This

procedure was repeated for the remaining cut samples.

The Percent Water Loss, Absorption and Effective Absorption were then calculated according to the following formulas:

Percent Water Loss = 100 * (A - B) / B;
Absorption (g water / dry weight) =(A - D) / D;
Effective Absorption (g water absorbed / m^2) = 32.292 * (A - C).

ABRASION TESTING

The hydrophobic latex emulsion which is present in the binder precursor dries and cures to form a polymer which generally is expected to have poorer abrasion resistance than that of PVA polymer alone. To illustrate the effect of added latex emulsion on abrasion resistance, abrasion testing was performed using a Taber Abraser Model 503 equipped with H22 Calibrade wheels with 500 g weights. Samples were prepared for abrasion testing by saturating them in tepid water and mechanically wringing the samples 4 times to remove all excess water. Destruction was recorded at the point where a visible hole (0.3 cm (1/8 inch) diameter) in the sample appeared.

EXAMPLES

The features and advantages of the articles of the invention are further illustrated in the following non-limiting examples.

COMPARATIVE EXAMPLE A

A red wiping article using the substrate described above in PROCEDURE A. It was coated with 139 g of PVA solution (prepared as described in PROCEDURE B) mixed with 0.6 g of an organic red pigment (commercially available as "Orcobrite Red BRYN 6002" from Organic Dye Stuffs of Charlotte, NC) and 61 g deionized water. The coated sample was dried and cured as described in PROCEDURE C.

COMPARATIVE EXAMPLE B

A blue wiping article was prepared using the substrate described above in

PROCEDURE A. It was coated with 139 g of PVA solution (prepared as described in PROCEDURE B) mixed with 0.5 g of an organic blue pigment (commercially available as "Orcobrite Blue 3GN 2010") and 61 g deionized water. The coated sample was dried and cured as described in PROCEDURE C.

COMPARATIVE EXAMPLE C

A green wiping article was prepared using the substrate described above in PROCEDURE A. It was coated with 139 g of PVA solution (prepared as described in PROCEDURE B) mixed with 0.3 g of an organic green pigment (commercially available as "Orcobrite Green YN 9") and 61 g deionized water. The coated sample was dried and cured as described in PROCEDURE C.

EXAMPLE 1

This example demonstrates the preparation of a red wiping article. The sample was prepared using the fiber web described in PROCEDURE A. It was coated with a binder precursor mixture prepared from 132 g PVA solution (as described in PROCEDURE B), 0.45 g of a latex emulsion ("Hycar T-278"), 0.6 g of an organic red pigment ("Orcobrite Red BRYN 6002") and 67 g deionized water. The coated sample was dried and cured as described in PROCEDURE C. The resultant wiping article contained 5 percent of the polymer derived from the latex emulsion ("Hycar T-278") in the binder based on dry solids.

EXAMPLE 2

This example demonstrates the preparation of a red wiping article. The sample was prepared using the fiber web described in PROCEDURE A . It was coated with a binder precursor mixture prepared from 125 g PVA solution (as described in PROCEDURE B), 0.91 g of a latex emulsion ("Hycar T-278"), 0.6 g of an organic red pigment ("Orcobrite Red BRYN 6002") and 74 g deionized water. The coated sample was dried and cured as described in PROCEDURE C. The resultant wiping article contained 10 percent of a polymer derived from the latex emulsion ("Hycar T-278") in the binder based on dry solids.

EXAMPLE 3

This example demonstrates the preparation of a red wiping article. The sample was

prepared using the fiber web described in PROCEDURE A. It was coated with a binder precursor mixture prepared from 118 g PVA solution (as described in PROCEDURE B), 1.36 g of latex emulsion ("Hycar T-278"), 0.6 g of an organic red pigment ("Orcobrite Red BRYN 6002") and 80 g deionized water. The coated sample was dried and cured as described in PROCEDURE C. The resultant wipe contained 15 percent of polymer derived from the latex emulsion ("Hycar T-278") in the binder based on dry solids.

EXAMPLE 4

This example demonstrates the preparation of a blue wiping article. The sample was prepared using the fiber web described in PROCEDURE A. . It was coated with a binder precursor mixture prepared from 125 g PVA solution (as described in PROCEDURE B), 0.91 g of latex emulsion ("Hycar T-278"), 0.5 g of an organic blue pigment ("Orcobrite Blue 3GN 2010") and 74 g deionized water. The coated sample was dried and cured as described in PROCEDURE C. The resultant wipe contained 10 percent of polymer derived from the latex emulsion ("Hycar T-278") in the binder based on dry solids.

EXAMPLE 5

This example demonstrates the preparation of a green wiping article. The sample was prepared using the fiber web described in PROCEDURE A. It was coated with a binder precursor mixture prepared from 125 g PVA solution (as described in PROCEDURE B), 0.91 g of latex emulsion ("Hycar T-278"), 0.3 g of an organic green pigment ("Orcobrite Green YN 9") and 74 g deionized water. The coated sample was dried and cured as described in PROCEDURE C. The resultant wipe contained 10 percent of polymer derived from the latex emulsion ("Hycar T-278") in the binder based on dry solids.

The detailed results of analytical testing of performance changes are given below in Table 1.

COMPARATIVE EXAMPLES A-C AND EXAMPLES 1-5

Tensile Test Results:

Tensile strength measurements were made as described in the test method for TENSILE STRENGTH, above. The tensile strength and elongation at break were measured in the machine (Direction 1) and cross web (Direction 2) direction of the sample. No significant deterioration of tensile properties was observed, indicating that there was little detrimental effect caused by the incorporation of a hydrophobic latex emulsion ("Hycar T-278").

Table 1
Tensile Testing

Example	Orientation	Load at Peak Maximum (lb/in)	Standard Deviation	% Elongation at Peak Maximum	Standard Deviation
C. Ex. A	Direction 1	29.8	1.9	60	2
"	Direction 2	38.1	2.5	75	3
1	Direction 1	35.5	0.7	68	4
"	Direction 2	38.4	1.2	76	3
2	Direction 1	30.6	1.4	70	4
"	Direction 2	37.3	1.8	75	3
3	Direction 1	32.9	1.2	63	8
"	Direction 2	41.2	2.5	78	4

Bleach Stability:

Wiping articles made according to Comparative Example A and Example 2 were tested for bleach stability according to the above Bleach Stability Test Method. When the samples were removed from the bleach solution, the immersed sample from Comparative Example A had faded in color level compared to non-immersed wiping articles from Comparative Example A, while the immersed sample from Example 2 remained vividly red, with less apparent color fading. No negative effects were observed on bleach stability using the latex additive.

Tensile Testing was conducted on these samples, both before and after exposure to the bleach solution. The data are reported in Table 2.

Table 2
Tensile Test
(Bleached Samples)

Sample	Orientation	Load at Peak Maximum (lb/in)	Standard Deviation	% Tensile Load Loss
Before bleach				
Comparative Example A	Direction 1	29.8	1.9	
	Direction 2	38.1	2.5	
2	Direction 1	30.6	1.4	
	Direction 2	37.3	1.8	
8 hrs in 2% bleach				
Comparative Example A	Direction 1	13.1	1.0	56
	Direction 2	15.2	1.0	61
2	Direction 1	17.3	0.9	43
	Direction 2	21.4	2.3	43

Tear Test Results:

Tear tests were conducted for the articles of Comparative Example A and Examples 1-3 as described in the ELMENDORF TEAR TEST, above. The data are set forth in Table 3. The data indicate that there is no deleterious effect on the tear resistance of the samples due to the presence of a polymer derived from a hydrophobic latex emulsion.

Table 3

Tear Test

Example	Orientation	Average	Standard Deviation
Comparative Example A	Direction 1	68	15
	Direction 2	89	7
Comparative Example A	Direction 1	76	15
	Direction 2	80	11
1	Direction 1	76	11
	Direction 2	73	14
2	Direction 1	69	10
	Direction 2	67	11
2	Direction 1	74	18
	Direction 2	76	16
3	Direction 1	74	14
	Direction 2	88	8

Absorption Testing:

Absorption testing according to the above ABSORPTION TESTING Method indicated no significant effect on absorption due to the presence of a polymer derived from a hydrophobic latex emulsion. The data are reported in Table 4.

Table 4
Water Absorption

Example	% Water Loss	Absorption (g water / g dry sample)	Effective Absorption (g water absorbed / ft^2)
Comparative Example A	16.54	6.42	90.57
Comparative Example A	16.16	5.79	84.00
Example 1	14.34	6.23	90.90
Example 2	17.42	6.39	97.95
Example 2	14.57	6.14	87.69
Example 3	17.60	6.41	87.96

Abrasion Testing

Samples were abraded according to the Abrasion Testing Method with destruction of the sample recorded at the point where a visible hole (0.32 cm (1/8 inch) diameter) appeared. The data are set forth in Table 5. The data indicate that there is no deleterious effect on the abrasion resistance of the samples due to the presence of a polymer derived from a hydrophobic latex emulsion.

Table 5
Abrasion Test

Example	Cycles to Destruction
Comparative Example A	1228
1	1126
2	1419
2	1677
3	1668

Color Bleed

Wiping articles were subjected to the color bleed test as follows. In the case of red, blue, and green wiping articles of the Comparative Examples A, B and C, heavy color bleed was observed with wringing in water, and severe color bleed was observed on wringing with detergent. In contrast, at most a faint color could be detected after wringing with detergent in the case of the wiping articles with 10 percent or more added latex. The results with 5 percent addition of the "Hycar T-278" latex were intermediate to the 0 and 10 percent levels.

The data are set forth in Table 6 at the wavelength of maximum color absorption for each sample.

Table 6
Color Bleed

Example	Wavelength (nm)	Absorption After Water Rinse	Absorption After Soap Rinse	percent Reduction In Color Bleed
Comparative Example A	525	0.4062	1.0285	NA
1	525	0.0377	0.1759	91
2	525	0.0149	0.0875	83
3	525	0.0093	0.1008	90
Comparative Example B	625	0.5034	0.8764	NA
4	625	0.0110	0.0374	96
Comparative Example C	650	0.2986	1.0900	NA
5	650	0.0318	0.0932	91

COMPARATIVE EXAMPLE D

A red wiping article was prepared using the substrate described above in PROCEDURE A. It was coated with 152 g of PVA solution prepared as described in PROCEDURE B mixed with 0.3 g of an organic red pigment (commercially available as "Orcobrite Red BRYN 6002") and 61 g deionized water. The coated sample was dried and cured as described in PROCEDURE C. The binder content of the resultant cured wiping article was 14 percent (based on dry solids).

EXAMPLE 6

A red wiping article was prepared using the fiber web as described in PROCEDURE A. It was coated with a binder precursor mixture prepared from 137 g PVA solution (as described in PROCEDURE B), 1.2 g of latex emulsion ("Rhoplex NW-1845", a non-crosslinking latex), 0.63 g of an organic red pigment ("Orcobrite Red BRYN 6002") and 61 g deionized water. The coated sample was dried and cured as described in PROCEDURE C. The binder content of the resultant cured wipe was 15 percent.

EXAMPLE 7

A red wiping article was prepared using the fiber web described in PROCEDURE A. It was coated with a binder precursor mixture prepared from 137 g PVA solution (as described in PROCEDURE B), 1.2 g of latex emulsion ("Rhoplex ST-954", an acrylic self-

crosslinking emulsion), 0.63 g of an organic red pigment ("Orcobrite Red BRYN 6002") and 61 g deionized water. The coated sample was dried and cured as described in PROCEDURE C. The binder content of the resultant cured wipe was 15 percent.

EXAMPLE 8

A red wiping article was prepared using the fiber web described in PROCEDURE A. It was coated with a binder precursor mixture prepared from 137 g PVA solution (as described in PROCEDURE B), 1.2 g of a styrene-butadiene self-crosslinking latex emulsion ("Unocal 4170"), 0.64 g of an organic red pigment ("Orcobrite Red BRYN 6002") and 61 g deionized water. The coated sample was dried and cured as described in PROCEDURE C. The binder content of the resultant cured wipe was 15 percent.

COMPARATIVE EXAMPLE D and EXAMPLES 6-8

The articles of Examples 6, 7, 8 and Comparative Example D were evaluated for color bleed according to the above Color Bleed Test Method. The observed color bleed of Examples 6, 7 and 8 was significantly less than that for Comparative Example D.

Although the preferred embodiment of the invention has been discussed and described in detail, it will be appreciated that changes and modifications to the described embodiment can be made by those skilled in the art without departing from the true spirit and scope of the invention, as set forth in the claims.

What is claimed is:

1. An absorbent article comprising:

(a) a substrate comprised of organic fibers having a plurality of pendant hydroxyl groups;

(b) a binder coated on at least a portion of the fibers, the binder comprising a crosslinked polyvinyl alcohol and a hydrophobic polymer; and

(c) pigment distributed within the binder.

2. The absorbent article of Claim 1, wherein the substrate comprises a nonwoven web.

3. The absorbent article of Claim 2, wherein the nonwoven web has a weight per unit area ranging from about 50 g/m^2 to about 250 g/m^2.

4. The absorbent article of Claim 1, wherein the organic fibers comprise materials selected from the group of polyvinyl alcohol and rayon.

5. The absorbent article of Claim 4, wherein the ratio of polyvinyl alcohol fibers to rayon fibers ranges from 30:70 to 70:30.

6. The absorbent article of Claim 1, wherein the polyvinyl alcohol is a silanol-modified polyvinyl alcohol.

7. The absorbent article of Claim 6, wherein the silanol-modified polyvinyl alcohol is crosslinked with a metal complex selected from the group of aluminum, titanium, silicon, and zirconium chelates and combinations of the foregoing.

8. The absorbent article of Claim 1, wherein the hydrophobic polymer is derived from a self-crosslinking latex emulsion.

9. The absorbent article of Claim 1, wherein the hydrophobic polymer is derived from a hydrophobic latex emulsion based on materials selected from the group of acrylate,

acrylic acid, methacrylic acid, acrylonitrile, styrene, *N*-methylolacrylamide, polyurethane, polyester, and polyamide.

10. The absorbent article of Claim 9, wherein the acrylate is selected from the group of butyl acrylate, ethyl acrylate, and methyl methacrylate.

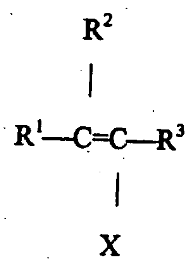
11. The absorbent article of Claim 1, wherein the hydrophobic polymer has a glass transition temperature of less than 0°C.

12. The absorbent article of Claim 1 wherein the hydrophobic polymer has a glass transition temperature of less than -15°C.

13. The absorbent article of Claim 1 wherein the hydrophobic polymer is present in the range of 1 to 15 weight percent of the binder.

14. The absorbent article of Claim 1, wherein the pigment is an organic pigment.

15. The absorbent article of Claim 1, wherein the polyvinyl alcohol is a hydrolyzed, crosslinked homopolymer or copolymer derived from the copolymerization of first and second monomers, the first monomer consisting of monomers within the general formula (I)



(I)

wherein X is $Si(OR^4OR^5OR^6)$; and

the second monomer consisting of monomers within the general formula (II)

$$\begin{array}{l} \quad\;\; R^2 \\ \quad\;\;\, | \\ R^1\text{—}C\text{=}C\text{—}R^3 \\ \qquad\quad\;\, | \\ \qquad\quad\;\, Y \end{array} \qquad\qquad (II)$$

wherein Y is $O(CO)R^7$; and R^1, R^2, R^3, R^4, R^5, R^6 and R^7 are independently selected from the group consisting of hydrogen and organic radicals having from 1 to about 10 carbon atoms.

16. The absorbent article of Claim 15, wherein the polyvinyl alcohol is crosslinked with a crosslinking agent selected from the group of aldehydes, diisocyanates, polyacrylic acid, metal complexes, and combinations of the foregoing.

17. The absorbent article of Claim 16, wherein the metal complexes are selected from the group of aluminum, titanium, silicon, and zironium chelates and combinations of the foregoing.

18. The absorbent article of Claim 15, wherein the polyvinyl alcohol is crosslinked via secondary hydroxyl groups on the polymer backbone using organic titanates as the crosslinking agent, and silanol groups on the polymer backbone are crosslinked using metal oxides as another crosslinking agent.

19. A method of making an absorbent article, the method comprising:

(a) providing a substrate comprising organic fibers having a plurality of pendant hydroxyl groups;

(b) coating at least a portion of the fibers with a mixture of a pigment and a binder precursor, the binder precursor comprising polyvinyl alcohol and a hydrophobic latex emulsion; and

(c) curing the binder precursor to provide an absorbent article.

20. The method of claim 19 wherein the providing step (a) further comprises providing the substrate in the form of a carded and crosslapped nonwoven web.

21. The method of claim 19 wherein the providing step (a) further comprises providing the substrate in the form of a nonwoven web having first and second major surfaces, and entangling the organic fibers within the nonwoven web by needletacking.

22. The method of claim 21, wherein the nonwoven web has a weight per unit area ranging from about 50 g/m^2 to about 250 g/m^2.

23. The method of claim 19 wherein the coating step (b) comprises coating at least one of the first and second major surfaces of the nonwoven web with the binder precursor.

24. The method of claim 19, wherein the organic fibers comprise materials selected from the group of polyvinyl alcohol and rayon.

25. The method of claim 24, wherein the ratio of polyvinyl alcohol fibers to rayon fibers ranges from 30:70 to 70:30.

26. The method of claim 19, wherein the hydrophobic latex emulsion comprises a self-crosslinking polymer.

27. The method of claim 19, wherein the hydrophobic latex emulsion is based on materials selected from the group of acrylate, acrylic acid, methacrylic acid, acrylonitrile, styrene, *N*-methylolacrylamide, polyurethane, polyester, and polyamide.

28. The method of claim 27 wherein the acrylate is selected from the group of butyl acrylate, ethyl acrylate, and methyl methacrylate.

29. The method of claim 19, wherein the hydrophobic latex emulsion is present in the range of 1 to 15 weight percent of the binder.

30. The method of claim 19, wherein the pigment is an organic pigment.

31. The method of claim 19, wherein the polyvinyl alcohol in the binder precursor is a homopolymer or copolymer derived from the copolymerization of first and second monomers, the first monomer consisting of monomers within the general formula (I)

$$\begin{array}{ccccc} & R^2 & & & \\ & | & & & \\ R^1 - & C & = & C & - R^3 \\ & & & | & \\ & & & X & \end{array} \qquad (I)$$

wherein X is $Si(OR^4OR^5OR^6)$; and

the second monomer consisting of monomers within the general formula (II)

$$\begin{array}{ccccc} & R^2 & & & \\ & | & & & \\ R^1 - & C & = & C & - R^3 \\ & & & | & \\ & & & Y & \end{array} \qquad (II)$$

wherein Y is $O(CO)R^7$; and R^1, R^2, R^3, R^4, R^5, R^6 and R^7 are independently selected from the group consisting of hydrogen and organic radicals having from 1 to about 10 carbon atoms.

32. The method of claim 31, wherein the binder precursor further comprises a crossllinking agent compatible with the polyvinyl alcohol, the crosslinking agent selected from the group of aldehydes, diisocyanates, polyacrylic acid, metal complexes, and combinations of the foregoing.

33. The method of claim 32, wherein the metal complexes are selected from the group of aluminum, titanium, silicon, and zirconium chelates and combinations of the foregoing.

34. The method of claim 31, wherein curing step (c) comprises a crosslinking reaction wherein the polyvinyl alcohol is crosslinked via secondary hydroxyl groups on the polymer backbone using organic titanates as the crosslinking agent, and silanol groups on the polymer backbone are crosslinked using metal oxides as another crosslinking agent.

35. An absorbent article comprising a substrate having first and second major surfaces, the substrate comprising organic fibers having a plurality of pendant hydroxyl groups, wherein at least one of the first and second major surfaces is coated with a mixture comprising:

(a) a binder comprising a crosslinked polyvinyl alcohol and a hydrophobic polymer; and

(b) pigment distributed within the binder.

36. The absorbent article of Claim 35, wherein the substrate comprises a nonwoven web.

37. The absorbent article of Claim 36, wherein the nonwoven web has a weight per unit area ranging from about 50 g/m^2 to about 250 g/m^2.

38. The absorbent article of Claim 36, wherein the organic fibers comprise materials selected from the group of polyvinyl alcohol and rayon.

39. The absorbent article of Claim 36, wherein the polyvinyl alcohol is a silanol-modified polyvinyl alcohol.

40. The absorbent article of Claim 39, wherein the silanol-modified polyvinyl alcohol is crosslinked with a metal complex selected from the group of aluminum, titanium, silicon, and zirconium chelates and combinations of the foregoing.

41. The absorbent article of Claim 36, wherein the hydrophobic polymer is derived from a hydrophobic latex emulsion based on materials selected from the group of acrylate, acrylic acid, methacrylic acid, acrylonitrile, styrene, *N*-methylolacrylamide, polyurethane, polyester, and polyamide.

42. The absorbent article of Claim 36, wherein the hydrophobic polymer is present in the range of 1 to 15 weight percent of the binder.

43. The absorbent article of Claim 36, wherein the pigment is an organic pigment.

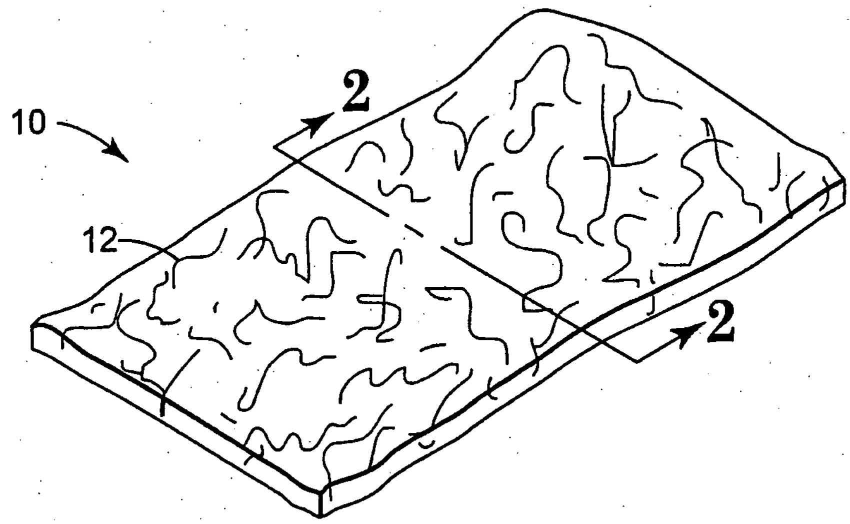


Fig. 1

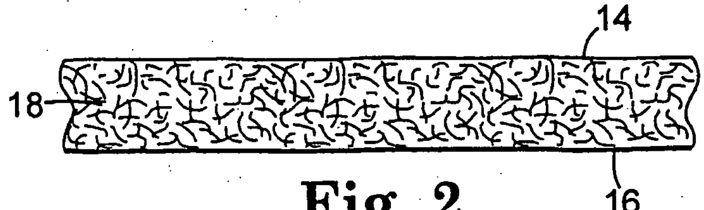


Fig. 2

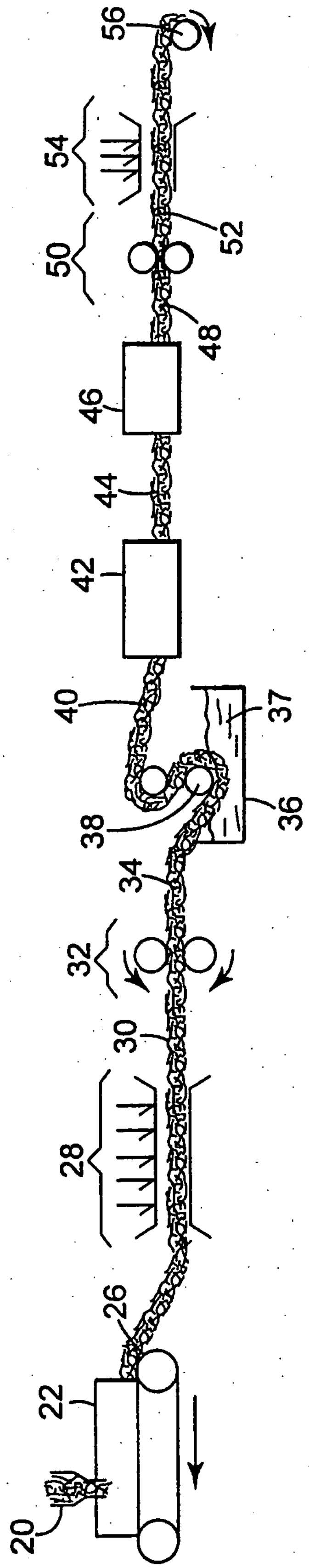


Fig. 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/13577

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D04H1/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D04H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 28223 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 8 December 1994 cited in the application see claims; example 91	1-43

[ ] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 April 1998	09/04/1998

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 97/13577

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9428223 A	08-12-1994	AU 680884 B	14-08-1997
		AU 6274194 A	20-12-1994
		BR 9406745 A	12-03-1996
		CA 2163109 A	08-12-1994
		CN 1124985 A	19-06-1996
		DE 69403797 D	17-07-1997
		DE 69403797 T	15-01-1998
		EP 0705354 A	10-04-1996
		JP 8510796 T	12-11-1996
		US 5641563 A	24-06-1997
		US 5656333 A	12-08-1997